

(12) UK Patent Application (19) GB (11)

2 035 335 A

- (21) Application No 7936174
(22) Date of filing 18 Oct 1979
(30) Priority data
(31) 53/130479
54/104102
(32) 25 Oct 1978
17 Aug 1979
(33) Japan (JP)
(43) Application published
18 Jun 1980
(51) INT CL³
C08J 7/14
(52) Domestic classification
C3L 160 JD
C3W 322
C3Y B287 F118
(56) Documents cited
None
(58) Field of search
C3L
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(54) Polyacetal resin composition excellent in heat stability and surface processability and process for surface treating same

(57) A polyacetal resin composition comprises (a) about 100 parts by weight of polyacetal resin (b) about 2 to about 35 parts by weight of carbonate, phosphate, acetate or their mixture of a metal belonging to Group II of the periodic table and (c) about 0.01 to about 20 parts by weight of polymer, copolymer or their mixture of a compound selected from unsaturated polyester, alkyl ester of (meth)acrylic acid, (meth)acrylamide, triallyl cyanurate, diallyl phthalate, vinyl acetate and divinylbenzene. Articles molded from this composition are surface-roughened by dipping the molded article into an aqueous solution containing sulfuric acid. After this treatment the surface of the molded article is receptive to a surface coating, such as electroplating.

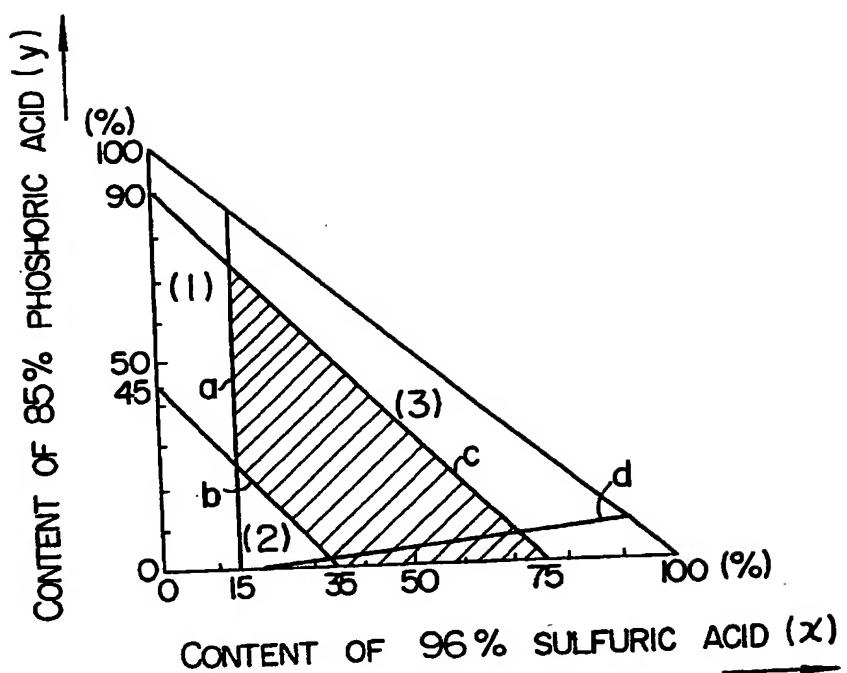
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FIG.



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SPECIFICATION

Polyacetal resin composition excellent in heat stability and surface processability and process for surface treating same

- 5 This invention relates to a polyacetal resin composition excellent in heat stability and surface processability. Generally speaking, plastics are quite stable chemically and their molded products by injection molding or the like have a smooth surface, so that their surface is difficult to be decorated by means of printing, coating, deposition or the like or to subject to a surface processing such as adhesion by means of adhesive. Since 10 polyacetal resin is particularly poor in surface activity and there is known no appropriate solvent having an affinity to polyacetal, its surface decoration and adhesion are difficult to practice and it is scarcely put to uses requiring such treatments at the present stage. Conversely speaking, since polyacetal resin is excellent in mechanical properties, it is mainly used as mechanical parts or the like in many cases and its surface decoration has not been required hitherto so frequently.
- 15 However, the application of plastics has intensely inclined to diversification and higher class usage in the recent time and it is frequently required to simultaneously satisfy plural performances, such as function and appearance or function and adhesion property, of which compatibility has not necessarily been required hitherto. Thus, it is the current trend to require good surface processability even in the application of polyacetal.
- 20 Though it is difficult to say that the process for improving surface processability of polyacetal has actively been studied hitherto, we are informed of the fact that the surface processability can be improved to some extent by treating the surface of molded product with an acidic solution of an oxidant solution. As said acidic solution, p-toluenesulfonic acid, comporphosulfonic acid, phosphoric acid, acid ammonium sulfate and the like were proposed, while as said oxidant solution chromic acid-sulfuric acid mixture was proposed.
- 25 The object of the treatment with these solutions is considered to consist in producing a rough surface by chemically etching the surface of molded product of polyacetal resin and simultaneously forming reactive groups on a part of polyacetal molecule by the oxidizing action of the solutions. In general, if it is attempted to enhance the effect of surface treatment in such a treatment, there rise troubles such as deterioration of parent material, i.e. polyacetal resin, throughout whole the body of molded article, a formation of crack, etc.
- 30 On the other hand, if the treatment is carried out under a condition causing no deterioration of parent material, the effect of surface treatment is insufficient and a good surface processing cannot be practised. For these reasons, there has hitherto been known no molded product of polyacetal resin having an enough surface processability for practical use.
- The present inventors earnestly studied the composition of polymer with the aim of obtaining a molded 35 product of polyacetal resin excellent in surface processability. As the result, it was found that a composition comprising polyacetal resin, a salt of a metal belonging to Group II of the periodic table and a certain kind of polymer exhibits excellent performances in heat stability and surface processability.
- Thus, this invention relates to a polyacetal resin composition excellent in heat stability and surface processability which comprises (a) about 100 parts by weight of polyacetal resin, (b) about 2 to about 35 40 parts by weight of carbonate, phosphate, acetate or their mixture of a metal belonging to Group II of the periodic table, and (c) about 0.01 to about 20 parts by weight of a polymer, copolymer or their mixture of a compound selected from unsaturated polyester, alkyl ester of acrylic or methacrylic acid, amide of acrylic or methacrylic acid, triallyl cyanurate, diallyl phthalate, vinyl acetate and divinylbenzene.
- In this invention, the object of adding a salt of a metal belonging to Group II of the periodic table to 45 polyacetal resin consists in facilitating the formation of roughened surface suitable for surface processing. That is to say, if a salt of a metal belonging to Group II of the periodic table is dispersed in the continuous phase of polyacetal, it can easily be decomposed and removed with an acid and the mark remains as a roughened surface.
- Examples of the metal belonging to Group II of the periodic table used in this invention include calcium, 50 magnesium, barium, zinc and the like, and examples of said salt include carbonate, phosphate, acetate and the like. Among the salts, the salts of calcium, magnesium and barium are preferable and carbonates of these metals are particularly preferable. Particularly, calcium carbonate is most preferable. Among the phosphates, hydrogen phosphates are most preferable.
- In the surface treatment, for example plating, of a resin, the specular character of surface and the adhesion 55 between the plated metal layer and the surface of a resin are frequently fundamentally important characteristics. Further, good heat stability at the time of molding is severely required sometimes. The inventors studied the relation between these characteristics and average particle size of various salts of metals belonging to Group II of the periodic table to reveal that the metallic salt deteriorates specular character and adhesion if the average particle size exceeds about 4.0 microns and it deteriorates adhesion 60 and heat stability if the average particle size is smaller than about 0.1 micron. Accordingly, if specular character, adhesion and heat stability are all taken into consideration, the average particle size of the salt of metal belonging to Group II of the periodic table is preferably in the range of about 0.1 to about 4.0 microns and particularly in the range of about 0.5 to about 2.0 microns.
- If the amount of salt of metal belonging to Group II of the periodic table is too small, the effect of improving 65 the surface processability cannot be exhibited. If it is too large, the mechanical characteristic properties of

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polyacetal resin are deteriorated and, simultaneously, the effect of improving surface processability rather drops and heat stability at the time of molding is also deteriorated. Considering these balance, therefore, the amount of the salt is preferably in the range of about 2 to about 35 parts by weight and more preferably in the range of about 2 to about 25 parts by weight per about 100 parts by weight of polyacetal resin.

5 On the other hand, the inventors conducted extensive studies about this polyacetal resin composition, i.e. various compositions comprising a polyacetal resin and various salts of metals belonging to Group II of the periodic table of which average particle size and amount are in the ranges defined above, to reveal that, in etching a molded product with an appropriate acid, i.e. an acidic solution or an oxidant solution, the molded product itself is cracked and specular character and mechanical performances of plated product are markedly deteriorated if the acidic or oxidant solution is particularly strong and that, if the condition of molding are not controlled sufficiently at the time of molding, the molded product can sometimes be discoloured and streaks of decomposition gas formed by the thermal decomposition of polyacetal resin at the time of molding can sometimes remain in the surface of the molded product.

The inventors conducted further studies with the aim of solving these problems. As the result, it was found 10 that the above-mentioned problems can be overcome by additional incorporating, into the above-mentioned polyacetal resin composition, a polymer, a copolymer or their mixture of a compound selected from unsaturated polyester, alkyl ester of acrylic acid or methacrylic acid, amide of acrylic acid or methacrylic acid, triallyl cyanurate, diallyl phthalate, vinyl acetate and divinylbenzene. Based on this finding, the present invention was accomplished.

15 20 As said unsaturated polyester, a product obtainable by esterifying an unsaturated dicarboxylic acid or its mixture with a saturated dicarboxylic acid or a saturated or unsaturated monocarboxylic acid with a polyhydric alcohol or its mixture with a monohydric alcohol can be used.

As the acid used for the production of said unsaturated polyester, maleic acid, maleic anhydride, fumaric acid, Itaconic acid, citraconic acid, endomethylenetetrahydrophthalic acid and the like can be used as said 25 30 acid, unsaturated dicarboxylic acid, and o-phthalic acid, phthalic anhydride, isophthalic acid, terephthalic acid, adipic acid and the like can be used as the saturated dicarboxylic acid. Mixtures of two or more members of them can also be used. As said monocarboxylic acid, acetic acid, propionic acid, butyric acid, benzoic acid, acrylic acid, methacrylic acid and the like can be used, and mixtures of two or more members of them can be used. The above-mentioned carboxylic acids may also be supplied in the form of alkyl ester such as methyl ester, dimethyl ester or the like.

As said polyhydric alcohol, ethylene glycol, propylene glycol, butanediol, diethylene glycol, dipropylene glycol, glycerin, trimethylolpropane and the like can be used. As said monohydric alcohol, methanol, ethanol, allyl alcohol and the like can be used.

An example of preferable unsaturated polyesters is an ester comprising isophthalic acid, maleic anhydride 35 40 and diethylene glycol.

Said unsaturated polyester, in order to facilitate its thermosetting, is frequently provided in the form of a mixture with a crosslinking agent having reactive unsaturated bond, such as, a vinyl monomer or a prepolymer having an unsaturated residue of vinyl group. As said crosslinking agent, styrene, α -methylstyrene, vinylpyridine, vinylpyrrolidone, vinyl propionate and the like can be used.

45 50 When styrene, α -methylstyrene, vinylpyridine, vinylpyrrolidone, vinyl propionate or the like is added as a crosslinking agent, its amount is preferably in the range of about 0.2 time to about 1.0 time the weight of unsaturated polyester or the total weight of unsaturated polyester and other compounds (as has been mentioned above, it is such a range that the weight of unsaturated polyester or the total weight of unsaturated polyester and other compounds becomes about 20 parts by weight or less per about 100 parts by weight of polyacetal resin). In case of using together with crosslinking agent, said amount of the unsaturated polyester means the amount including that of the crosslinking agent used.

In the component (c) of this invention, when said unsaturated polyester is copolymerized or mixed with other compounds, their proportion may be selected arbitrarily.

As said alkyl ester of acrylic acid or methacrylic acid, those of which alkyl group has 1-5 carbon atoms and 55 60 preferably 1-2 carbon atoms can be used recommendably.

In this invention, accordingly, the abovementioned component (c) to be incorporated into polyacetal resin (a) together with the salt of metal belonging to Group II of the periodic table (b) constitutes an indispensable constructional condition of the invention. The object of adding component (c) will be again summarized hereunder. It is added for the purpose of preventing a molded product from crack formation even when the etching is carried out with a particularly strong acidic solution or oxidant solution and, at the same time, for the purpose of preventing the deterioration of heat stability at the time of molding which may occur when a salt of metal belonging to Group II of the periodic table is added to polyacetal resin.

Though the reason why the cracking at the time of etching can be prevented is not known clearly, it seems to be as follows. When a salt of a metal belonging to Group II of the periodic table is added to polyacetal 65 70 resin, the composition obtained is rigid and has an increased internal strain. When the above-mentioned component (c) is added thereto, the internal strain becomes smaller or disappears owing to a plasticizer-like action of component (c), so that the formation of crack can be prevented.

Though the amount of component (c) used in this invention varies depending on its kind, it is preferably used in an amount of about 0.01 to about 20 parts by weight and more preferably in an amount of about 0.01 80 85 to about 15 parts by weight per about 100 parts by weight of polyacetal resin. If its amount is less than about

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0.01 part by weight, the abovementioned effect is not achievable. If its amount exceeds about 20 parts by weight, the overall strength and other characteristic properties of the compositon are deteriorated.

The polyacetal resin used in this invention may be a homopolymer, i.e. a polymer obtainable by polymerizing formaldehyde or trioxan (including those subjected to the end group stabilization treatment) or 5 binary, ternary or higher order copolymers obtained by copolymerizing trioxan with comonomers such as cyclic ether, cyclic acetal or the like.

It is allowable to add, to the composition of this invention, various additives usually added to polyacetal resin such as heat stabilizer, antioxidant, ultraviolet absorber, antistatic agent, crystalnucleating agent, pigment and the like.

10 In obtaining the composition of this invention, it is preferable to blend together the constitutional components by the use of an apparatus conventionally employed for kneading resin melts, such as kneader, roll mill, extruder and the like. From the viewpoint of interception of oxygen and work environment, the use of extruder is most recommendable.

The temperature of blending is not lower than the melting point of polyacetal resin used. This is 15 determined from the necessity to effect the blending of polyacetal resin uniformly in a molten state. Upper limit of the temperature is usually carried out at about 250°C or below, preferably at about 230°C or below.

Component (c) used for the sake of heat stabilization and prevention of crack, such as unsaturated polyester, may be directly blended as a polymer or a copolymer, or it may be added in the state of a monomer or a prepolymer and then polymerized in an extruder. In the case of thermosetting type of 20 polymers, the latter method is more preferable.

From the viewpoint of producing a composition of uniform quality, it is preferable to beforehand subject the individual constitutional components to a preliminary blending by means of tumbler or Henschel mixer. Further, from the viewpoint of stabilizing the feed into an extruder, it is more preferable to use the polyacetal resin in a powdered state. However, these are not indispensable conditions.

25 In the above-mentioned method in which a monomer or a prepolymer is added, it is preferable to keep the temperature of preliminary blending at a value causing no polymerization.

In the above-mentioned method in which a monomer or a prepolymer is added, a temperature of about 190°C and a duration of about 1 to about 10 minutes are necessary as an example of the conditions of heating enough to polymerize them, though the conditions may vary depending on the kind of monomer or 30 prepolymer. Such conditions are attainable in most cases by combining the temperature and duration conventionally employed for blending a polyacetal resin composition by means of a conventional extruder (they are dependent on the speed of extrusion), and no auxiliary heating means is necessary. In this invention, the heating means itself is not limited.

It is also allowable to incorporate a polymerization initiator into the composition.

35 By the above-mentioned heating, the monomer or prepolymer added is brought into polymerization. At this time, there are many methods for ascertaining that nothing is left unreacted. Among them, a simple method is to judge it from the odor of the mixture just after being heated and extruded (usually pelletformed). Another method adoptable is to dip the pellet in a solvent and to check the extraction of unreacted matter by means of infrared spectroscopy.

40 The pellet of polyacetal resin composition of this invention, produced by the above-mentioned process, is then molded into any desired shape by the conventional molding means such as injection molding, extrusion molding, compression molding or the like. Said molded product has an excellent surface processability. It is subjected to a surface roughening treatment with an appropriate solution mentioned later, after which it is put to use of electro-plating, coating or the like to display its excellent characteristic 45 properties;

As the appropriate solution used for the surface roughening treatment of the molded product obtained from the polyacetal resin composition of this invention, any solution may be used so far as it is an acidic solution or an oxidant solution capable of decomposing the metallic salt present in the composition. From the viewpoint of workability, less volatile solutions such as aqueous solution of sulfuric acid, mixed aqueous 50 solution of sulfuric acid and phosphoric acid, mixed aqueous solution of sulfuric acid and potassium bichromate and the like are used.

When the polyacetal resin is constituted of a copolymer, the surface roughening can sufficiently be carried out with aqueous solution of sulfuric acid, mixed aqueous solution of sulfuric acid and potassium bichromate, or the like. When the polyacetal resin is constituted of a homopolymer, there is an intense 55 tendency that the roughening of surface progresses in an ideal manner. When a mixed aqueous solution of sulfuric acid and phosphoric acid is used, the roughening of surface progresses satisfactorily whether the polyacetal is a copolymer or a homopolymer, though the progress is particularly satisfactory in the case of homopolymer. When a mixed aqueous solution of sulfuric acid and phosphoric acid is used, the proportion defined by the range shown in the attached drawing is preferable. Hereunder, using 96% sulfuric acid and 60 85% phosphoric acid, this will be explained with reference to a sulfuric acid-phosphoric acid concentration diagram.

The drawing attached is a diagram representing the concentrations of sulfuric acid and phosphoric acid in the etching acid solution, wherein abscissa is the content (%) of 96% by weight sulfuric acid based on water and ordinate is the content (%) of 85% by weight phosphoric acid based on water, for convenience.

65 The scope of concentration of the aqueous etching solution used in this invention will be explained with

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reference to the drawing showing the area surrounded by the straight line connecting the 100% point of 96% sulfuric acid on abscissa and the 100% point of 85% phosphoric acid on ordinate and the two axes. This area can be divided into the following parts:

(1) The left-side part of line a: Adhesion force, i.e. the peeling strength (kg/cm) of plated metal layer 5 formed after etching and by subsequent plating process, is so low as less than 1 kg/cm. In the figure, this corresponds to the low sulfuric acid concentration region residing in the left side of the line a denoting 15% by weight of 96% sulfuric acid.

(2) The under side of line b: The etching time for giving maximum adhesion is too long (more than 150 minutes is necessary at 40°C) so that productivity is poor. In the figure, this corresponds to the region 10 residing in the left-down side of the straight line b connecting 35% by weight point of 96% sulfuric acid and 45% by weight point of 85% phosphoric acid.

(3) The upper side of line c: The etching time for giving maximum adhesion is too short (1 minute or less at 40°C) so that stability is poor. In the figure, this corresponds to the region residing in the right-upper side of the straight line c connecting the 75% by weight point of 96% sulfuric acid and the 90% by weight point of 15 85% phosphoric acid.

All the above-mentioned regions (1), (2) and (3) are unemployable industrially, and the region other than (1), (2) and (3), i.e. the shadowed region which is surrounded by lines a, b and c in the figure, is the industrially employable region of this invention. When expressing the contents of said 96% sulfuric acid and 85% phosphoric acid by "x" and "y", respectively, the shadowed region is the range limited by the formulae,

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$$x \geq 15, y \geq -\frac{9}{7}x + 45 \text{ and } y \leq -\frac{6}{5}x + 90.$$

Further, an aqueous solution having the total content of said 96% sulfuric acid and 85% phosphoric acid 25 being 45 to 75% by weight and the content of said 96% sulfuric acid being 15% by weight is preferable, and furthermore, in the shadowed region, the upper side

25

$(y \geq \frac{1}{7}x - \frac{20}{7})$ of the straight line d connecting the point of 20% by weight of 96% sulfuric acid and the point of 90% by weight of 96% sulfuric acid and 10% by weight of 85% phosphoric acid is particularly preferable.

30 The sulfuric acid and the phosphoric acid used in this invention may be usually commercialized ones. As to sulfuric acid, that having a concentration of 96% is usually available, while as to phosphoric acid that having a concentration of 85% is usually available. The concentration area of this invention has been determined on these bases. When sulfuric acid and/or phosphoric acid having a different concentration is to be used, it is necessary to use the acid or acids after re-calculation on the basis of its actual concentration.

30

35 Next, as examples of use of the molded product obtained from the composition of this invention, electroplating process and coating process will be illustrated.

35

The electroplating of molded plastic articles has extensively been known hitherto and is industrially employed in the case of ABS or the like. These disclosed processes may also be applied to the electroplating of the polyacetal resin composition of this invention. For example, each process is carried out in the 40 following manner according to the description of Modern Plastics Encyclopedia, pp. 1019-1021 (1967):

40

(1) Defatting of molded article: The object of this process is to remove the fat of human hand or the mechanical oil adhering on the surface of molded article. This is carried out by dipping or vapor defatting with 1,1,1-trichloroethane. Defatting with conventional detergent is also possible.

(2) Surface roughening: A molded article is immersed in the above-mentioned acid. Though the 45 conditions of immersion vary with kind of molded article and composition of acid, the combination of temperature and time is selected so that the final plated product can have an excellent appearance (specular character) and around maximum and stable peeling strength. Some examples are shown in the Examples.

45

(3) Endowment of electrical conductivity (sensitizing, activation and electroless plating): The roughened 50 surface thus obtained is dipped in an aqueous HC1 solution containing SnCl_2 and then in an aqueous HC1 solution containing SnCl_2 and then in an aqueous HC1 solution containing PdCl_2 . According to a more preferable process adoptable, it is dipped in a mixed aqueous HC1 solution containing SnCl_2 and PdCl_2 in one step. Thus, nuclei of Pd are deposited on the roughened surface, around which a thin layer of nickel is formed chemically at the next process. Thus, an electrical conductivity is given to the surface of molded article.

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55 (4) Electroplating: Electroplating is carried out to a thickness fit for the use according to the usual method in the order of, for example, Cu/Ni/Cr.

55

When the polyacetal resin molded product having an excellent surface processability is etched and electro-plated in the above-mentioned manner, the adhesion or peeling strength of the plated layer is about 60 1 kg/cm or more and usually about 1.5 to about 2.5 kg/cm. The etched article also shows a surprising effect in the case of other than metal plating, namely in the case of coating or adhesion with adhesive, which demonstrates the usefulness of the polyacetal resin composition of this invention.

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Next, the coating process will be illustrated. The molded article is defatted and surface-roughened by the same or similar process as in electroplating, after which the surface is thoroughly dried. Then general coating materials are applied and baked for an appointed period of time.

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65 This invention will be illustrated more concretely by the following examples.

Examples 1-13 and Comparative Examples 1-2

100 parts by weight of polyacetal resin "Tenac [®]5010" (manufactured by Asahi Kasei Kogyo Co., acetal homopolymer, general grade) was mixed with 8.7 parts by weight of finely powdered calcium carbonate (manufactured by Shiraishi Calcium Co., average particle size 1.25 microns) and a quantity shown in Table 1 5 of component (c) compound by means of tumbler, after which the mixture was kneaded and pelletized by means of an extruder set at 190°C. By using the pellet, its heat stability was measured and, at the same time, a plaque of $\frac{1}{8}$ " thick was prepared by injection molding as a sample material.

The plaque was defatted with 1,1,1-trichloroethane and then etched by dipping it in a solution comprising 96% sulfuric acid/85% phosphoric acid/water = 40/25/35 (wt %) at 40°C for 8 minutes.

10 Then, the etched plaque was plated in the usual manner. Namely, it was dipped for an appointed period of time in a pretreatment solution for plastic plating (manufactured by Okuno Seiyaku Kogyo Co., "Catalyst") and then an accelerator (10% aqueous solution of hydrochloric acid), after which it was chemically plated with a chemical plating solution (manufactured by Okuno Seiyaku Kogyo Co., TMP chemical nickel plating solution) according to the appointed method and then immediately subjected to electroplating. The average 15 thicknesses of the plated metal layers were copper 40 microns, nickel 10 microns and chromium 0.1 micron. Performances of the plated product thus obtained were as shown in Table 1. The performances were measured by the following methods:

(1) Peeling strength of plated product: Two parallel breaking lines, 10 mm apart, were drawn on the plated surface, and the plated metal layer between the breaking lines was stretched to the right angle 20 direction of the flat plate to measure the stress necessary for peeling.

(2) Appearance of plated product: Under a light source of 300 luxes or more, the appearance was examined by the naked eye at a distance of 60 cm from the test surface. The criterion of the evaluation was as shown in the foot note of Table 1.

As is understandable from Table 1, the polyacetal resin composition of this invention is improved in heat 25 stability and excellent in plating characteristics.

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TABLE 1

	Comparative Example 1	Comparative Example 2	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
Polyacetal resin (Tenac® 5010) (parts by wt.)	100	100	100	100	100	100	100	100	100
Calcium carbonate (av. particle size 1.25 μ) (parts by wt.)	0	8.7	8.7	8.7	8.7	8.7	8.7	8.7	8.7
Compound (parts by wt.)	0	0	Unsat- rated polyester (Note 5) 0.87	Methyl acrylate 0.01	Ethyl acrylate 0.76	Methyl meth- acrylate 0.87	Ethyl meth- acrylate 0.01	Methyl acryl- amide (odor)	Meth- acryl- amide (odor)
Heat stability (Note 1)	②	△	②	○	○	○	○	②	②
Residual unreacted compound			None	None	None	None	None	None	None
Method of detection (solvent extraction or odor)			(Methanol/ toluene)	(Meth- anol)	(Meth- anol)	(Meth- anol)	(Meth- anol)	(odor)	(odor)
Appearance of plated product (Note 2)	x	x	○	○	○	○	○	○	○
Peeling strength of plated product (kg/cm)	0.2	2.2	2.3	1.6	1.8	1.7	1.6	2.0	2.1

TABLE I cont

- (Note 1) Injection molding can be carried out quite satisfactorily under usual conditions.
 Injection molding is possible without practical problems though the range of suitable
 conditions are somewhat narrow.
 At the time of injection molding, streaks are formed due to decomposition of resin. 5
 Extrusion is impossible
- (Note 2) Appearance was evaluated by the naked eye according to the following criterion:
 The so-called mirror surface having no crack.
 Obscure image though the face is reflected; no crack.
 No reflected image of face; crack formed.
- 10 (In the following Tables, same symbols as above have the same meanings as above.) 10
- (Note 3) 0.20 part by weight (Example 8) and 0.04 part by weight (Example 9) of 2,5-dimethyl-2,5-di(t-butylperoxy)-hexane was added as polymerization initiator.
- (Note 4) Degree of polymerization 200 (Nihon Gosei Kagaku Kogyo Co.); the other compounds were of chemically pure grade.
- 15 (Note 5) Upica [®]CLC-834 (manufactured by Toyo Boseki Co.) 15

Examples 14-17 and Comparative Examples 3-4

100 Parts by weight of polyacetal resin "Tenac [®]5010" (manufactured by Asahi Kasei Kogyo Co., acetal homopolymer, general grade) was mixed with 8.7 parts by weight of magnesium carbonate (average particle size 2-3 microns), barium carbonate (average particle size 2 microns), barium acetate (average particle size 3 20 microns) or calcium hydrogen phosphate (average particle size 2-3 microns) in place of the calcium carbonate, and as a reactive compound, an appointed quantity of unsaturated polyester [a mixture comprising 70 parts by weight of a polyester prepolymer, which was produced from isophthalic acid/maleic anhydride/diethylene glycol (= 1 mole/1 mole/2 moles) and has an average polymerization degree of 10, and 25 30 parts by weight of styrene as cross-linking agent] by means of a tumbler, after which the mixture was kneaded and pelletized by means of an extruder in the same manner as above.

The heat stability of this pellet was measured and, at the same time, a plaque was made therefrom and plated by the same process as in Example 1 to investigate the performances of plated product.

Heat stabilities of these polyacetal resin compositions and the performances of the plated products were 30 as shown in Table 2.

(All the above-mentioned metallic salts were of chemically pure grade. Barium acetate was used after pulverization in a mortar, while the other were used as they are.)

TABLE 2

	Comparative Example 3	Example 14	Comparative Example 4	Example 15	Example 16	Example 17
Polyacetal resin (Tenac E5010) (parts by wt.)	100	100	100	100	100	100
Magnesium carbonate (Av. particle size 2 - 3 μ) (parts by wt.)	8.7	8.7	-	-	-	-
Barium carbonate (Av. particle size 2 μ) (parts by wt.)	-	-	8.7	8.7	-	-
Barium acetate (Av. particle size 3 μ) (parts by wt.)	-	-	-	-	8.7	-
Calcium hydrogen phosphate (Av. particle size 2 - 3 μ) (parts by wt.)	-	-	-	-	-	8.7
Unsaturated polyester (parts by wt.)	-	-	8.7	Good	Violent foaming	Good
Extrudability	x	-	x	Good	Good	Good
Heat stability	-	-	○	○	○	○
Appearance of plated product	-	-	○	-	○	○
Peeling strength of plated metal layer (kg/cm)	-	-	1.8	-	1.7	1.6
					-	1.7

Examples 18-20 and Comparative Examples 5-6

100 Parts by weight of polyacetal resin "Tenac 5010" (manufactured by Asahi Kasei Kogyo Co.) was mixed with 11.1 parts by weight of calcium carbonate (manufactured by Shiraishi Calcium Co.) having the various average particle size shown in Table 3 and 1.1 parts by weight of unsaturated polyester 5 (manufactured by Toyo Boseki Co.). The resin composition obtained was plated by the same method as in Example 1, and performances of the plated products were investigated.

Performances of these plated products were as shown in Table 3.

TABLE 3

No.	Comparative Example 5*	Example 18	Example 19	Example 20**	Comparative Example 6
Average particle size 15 of calcium carbonate (micron)	0.08	1.0	1.25	3.6	5.0
Heat stability	x	○	◎	◎	◎
20 Appearance	-	○	○	△	x
Peeling strength (kg/cm)	-	2.0	2.0	1.5	1.0

25 * Extrusion was impossible.

** It is applicable to uses for which good appearance is not necessarily required.

Examples 21-23 and Comparative Example 7

The same etched plaque as in Table 3 was used. After being etched, it was thoroughly washed with water, 30 air-dried, coated with an acrylic coating material (manufactured by Tokyo Paint Co.) and then baked at 150°C for 30 minutes. Adherence of coated film was tested by pressing a strip of pressure sensitive transparent adhesive tape over an area of the surface which was cross hatched with $\frac{1}{8}$ " squares and then stripping the tape away. The results are shown in Table 4.

TABLE 4

No.	Example 21	Example 22	Example 23	Comparative Example 7
40 Average particle size of calcium carbonate (micron)	1.0	1.25	3.6	5.0
Adherence of coating film	◎	◎	○	x
45 Gloss	Glossy	Glossy	Glossy	Not glossy

Criterion for the evaluation of adherence test:

- ◎ No change occurs at all.
- Partial peeling occurs at corner parts.
- x Percentage of peeled squares is 20% or less
- xx Almost all the squares are peeled.

Examples 24-27 and Comparative Examples 8-10

55 Using the same calcium carbonate as in Example 1 (average particle size 1.25 microns), plating was carried out by the same method as in Example 1, provided that the amount of calcium carbonate was varied as shown in Table 5 and unsaturated polyester was added in an amount corresponding to 10% of the amount of calcium carbonate (parts by weight). The results are shown in Table 5.

TABLE 5

No.	Comparative Example 8	Comparative Example 9	Example 24	Example 25	Example 26	Example 27	Comparative Example 10
Polyacetal resin (Tenac®5010) (parts by wt.)							
Calcium carbonate (Av. particle size 1.25 μ) (parts by wt.)	0	1	3.1	8.7	17.6	26.0	42.9
Unsaturated polyester (parts by wt.)	0	0.1	0.31	0.87	1.76	2.5	4.3
Heat stability	①	②	③	④	⑤	⑥	x
Tensile strength (kg/cm ²)	700	700	690	650	600	580	-
Performances before plating	Tensile elongation (between chucks, %)	18	17	16	12	9	8
	Flexural strength (kg/cm ²)	1,050	1,050	1,040	1,040	1,030	1,020
Izod impact strength (notched,) kg.cm/cm	6	6	5	5	4	4	-
Appearance of plated product	x	x	0	0	0	0	-
Peeling strength of plated metal layer (kg/cm)	0.7	0.9	1.5	2.3	2.3	2.0	-

(Note) In Comparative Example 10, the resin decomposed when extruded.

Examples 28-31 and Comparative Examples 11-12

The experiment of Examples 25-27 and Comparative Example 8 was repeated, except that "Duracon[®] M90-02" (manufactured by Polyplastics Co., acetal copolymer, general grade) was used as polyacetal resin. The results are shown in Table 6.

TABLE 6
Comparative Example 11 **Example 28** **Example 29** **Example 30** **Example 31** **Comparative Example 12**

Polyacetal resin (Duracon [®] M90-02) (parts by wt.)	100	100	100	100	100	100
Calcium carbonate (Av. particle size 1.25 μ) (parts by wt.)	0	8.7	17.8	25.0	33.3	42.9
Unsaturated polyester (parts by wt.)	0	0.87	1.76	2.50	3.33	4.29
Heat stability	◎	◎	◎	○	○	△
Appearance of plated product	0	0	0	△	△	X
Peeling strength of plated metal layer (kg/cm)	0.2	1.3	2.1	1.8	1.5	1.0

DRAFT FINAL ADDENDUM

Examples 32-34 and Comparative Example 13

The experiment of Example 25 was repeated, except that the amount of unsaturated polyester was varied. The results are shown in Table 7.

TABLE 7

	Example 32	Example 33	Example 34	Comparative Example 13
Polyacetal resin (Tenac 6010) (parts by wt.)	100	100	100	100
Calcium carbonate (Av. particle size 1.25 μ) (parts by wt.)	8.7	8.7	8.7	8.7
Unsaturated polyester (parts by wt.)	0.87	10	15	25
Heat stability	⑥	0	0	x
Tensile strength (kg/cm ²)	650	600	570	520
Tensile elongation (between chucks, %)	12	13	13	14
Flexural strength (kg/cm ²)	1,040	900	850	740
Izod impact strength (notched, kg-cm/cm)	5	4	3	2

Examples 35-40 and Comparative Examples 14-18

The same plaque having a thickness of 3 mm as in Example 1 was plated in the same manner as in Example 1, provided that the composition of etching solution was varied as shown in Table 8. Peeling strengths of the plated metal layers obtained were as shown in Table 8.

	Example 35	Example 36	Example 37	Example 38	Example 39	Example 40	Example 14	Example 15	Example 16	Example 17	Example 18
96% sulfuric acid/ 85% phosphoric acid (parts by wt.)*	40/25	30/35	32/10	25/55	45/0	60/0	20/0	10/15	20/15	76/24	80/0
Optimum etching time (40°C X min.)	8	8	70	3	50	4	800	1,000	600	1	1
Peeling strength (kg/cm)	2.2	2.0	1.6	2.0	1.6	1.6	1.0	0.4	1.1	1.9	1.4

* When the sum of parts by weight was less than 100, water was added till the total weight reached 100 parts by weight.

Example 41

The same plaque having a thickness of 3 mm as in Example 29 was dipped in an etching solution having the following composition at 40°C for 12 minutes and then subjected to electroplating by repeating the steps mentioned in Example 29. Peeling strength of the plated metal layer obtained was 1.3 kg/cm.

5

Composition of etching solution:

10	96% sulfuric acid potassium bichromate water	55 parts by weight 4 parts by weight 45 parts by weight	10
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As is understandable from the examples mentioned above, the polyacetal composition of this invention is excellent in heat stability and, when its molded product is etched with an appropriate acid, it gives a molded product excellent in surface processability, so that the application field of the resin is further expanded. For example, it is substitutive for metals in the parts of which both functional and decorative characters are required. Thus, its effect of weight reduction and cost saving is very great.

CLAIMS

- 20 1. A polyacetal resin composition excellent in heat stability and surface processability which comprises (a) about 100 parts by weight of polyacetal resin, (b) about 2 to about 35 parts by weight of carbonate, phosphate, acetate or their mixture of a metal belonging to Group II of the periodic table and (c) about 0.01 to about 20 parts by weight of polymer, copolymer or their mixture of a compound selected from unsaturated polyester, alkyl ester of acrylic acid or methacrylic acid, amide of acrylic acid or methacrylic acid, triallyl cyanurate, diallyl phthalate, vinyl acetate and divinylbenzene.
- 25 2. A polyacetal resin composition according to Claim 1, wherein said metal belonging to Group II of the periodic table is calcium, magnesium or barium.
- 30 3. A polyacetal resin composition according to Claim 1, wherein said salt of metal belonging to Group II of the periodic table has an average particle size of about 0.1 to about 4.0 microns.
- 35 4. A polyacetal resin composition according to Claim 1, wherein said salt of metal belonging to Group II of the periodic table is calcium carbonate having an average particle size of about 1.25 microns.
- 40 5. A polyacetal resin composition according to Claim 1, wherein said alkyl ester of acrylic acid or methacrylic acid is methyl ester or ethyl ester.
- 45 6. A composition according to Claim 1, wherein said polyacetal resin contains a heat stabilizer, an antioxidant, an ultraviolet absorber, an antistatic agent, a crystal-nucleating agent or a pigment.
- 50 7. A process for roughening the surface of a molded product constituted of a polyacetal resin composition excellent in heat stability and surface processability and comprising (a) about 100 parts by weight of polyacetal resin, (b) about 2 to about 35 parts by weight of carbonate, phosphate, acetate or their mixture of a metal belonging to Group II of the periodic table and (c) about 0.01 to about 20 parts by weight of polymer, copolymer or their mixture of a compound selected from unsaturated polyester, alkyl ester of acrylic acid or methacrylic acid, amide of acrylic acid or methacrylic acid, triallyl cyanurate, diallyl phthalate, vinyl acetate and divinylbenzene, which comprises dipping said molded product in an aqueous solution containing sulfuric acid.
- 55 8. A process for roughening the surface according to Claim 7, wherein said aqueous solution containing sulfuric acid has a sulfuric acid concentration of 35% by weight to 75% by weight.
- 60 9. A process for roughening the surface according to Claim 7, wherein said aqueous solution containing sulfuric acid additionally contains phosphoric acid.
- 65 10. A process for roughening the surface of a molded product of polyacetal resin according to Claim 9, wherein the composition of sulfuric acid, phosphoric acid and water is represented, in a sulfuric acid-phosphoric acid-water concentration diagram, by the region which is in the right side of line a expressing 15% by weight of 96% sulfuric acid, in the upper side of straight line b connecting the point of 35% by weight aqueous solution of 96% sulfuric acid and the point of 45% by weight aqueous solution of 85% phosphoric acid, and in the down side of straight line c connecting the point 75% by weight aqueous solution of 96% sulfuric acid and the point of 90% by weight aqueous solution of 85% phosphoric acid.
- 70 11. A process for roughening the surface according to Claim 7, wherein said aqueous solution containing sulfuric acid additionally contains potassium bichromate.
- 75 12. A process for roughening the surface according to Claim 9, wherein the roughening is carried out with a solution having a composition of sulfuric acid/phosphoric acid/water = about 40/about 25/about 35, as expressed by parts by weight.
- 80 13. A process for roughening the surface according to Claim 7 substantially as described in any one of the Examples.
- 85 14. A molded product having a roughened surface obtained by a process according to any one of Claims 7 to 13.
- 90 15. A process according to anyone of Claims 7 to 13 further comprising electroplating or coating the roughened surface of the molded product.

16. A molded product which has been electroplated or coated by a process according to Claim 15.
17. A polyacetal resin composition according to Claim 1 substantially as described in any one of the Examples.
18. A molded product obtained by molding a polyacetal resin composition according to any one of Claims 1 to 6 or Claim 17.

Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon Surrey, 1980.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.